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(54) Titre : GRANULES DE CERAMIQUE A HAUTE RESISTANCE, RESISTANT A LA CHALEUR ET A LA CORROSION,
POUR AGENTS DE SOUTENEMENT

(54) Title: HIGH STRENGTH, HEAT- AND CORROSION-RESISTANT CERAMIC GRANULES FOR PROPPANTS

(57) Abrégé/Abstract:

The present invention describes a method for producing bulk, particulate high crush strength, and inert ceramic materials with a quasi-spherical shape prepared from raw oxide residues. These oxide residues are produced from the regeneration of spent acids based on a pyro-hydrolysis process, and/or as by-products from mineral processing and ore beneficiation operations. The final solid granules are obtained from the thermal treatment of previous raw oxide residues by several ceramics processing routes. These routes use common granulation processes well known in the ceramics industry. The final solid particles which exhibit both a high crushing strength, a low density, an elevated corrosion resistance in both brines, and acidic media, high indicia of sphericity and roundness are extremely suitable to be used in numerous industrial applications requiring inert and crush resistant quasi-spherical granules. Among these applications, owing to their excellent mechanical, thermal properties, and chemical inertness the granules can be used competitively as propping agent in the oil well production, and in a lesser extend due to their refractory behaviour as foundry sands in the metallurgical industry.

ABSTRACT

The present invention describes a method for producing bulk, particulate high crush strength, and inert ceramic materials with a quasi-spherical shape prepared from raw oxide residues. These oxide residues are produced from the regeneration of spent acids based on a pyro-hydrolysis process, and/or as by-products from mineral processing and ore beneficiation operations. The final solid granules are obtained from the thermal treatment of previous raw oxide residues by several ceramics processing routes. These routes use common granulation processes well known in the ceramics industry. The final solid particles which exhibit both a high crushing strength, a low density, an elevated corrosion resistance in both brines, and acidic media, high indicia of sphericity and roundness are extremely suitable to be used in numerous industrial applications requiring inert and crush resistant quasi-spherical granules. Among these applications, owing to their excellent mechanical, thermal properties, and chemical inertness the granules can be used competitively as propping agent in the oil well production, and in a lesser extend due to their refractory behaviour as foundry sands in the metallurgical industry.

HIGH STRENGTH, HEAT- AND CORROSION-RESISTANT CERAMIC GRANULES FOR PROPPANTS AND FOUNDRY SANDS AND METHOD FOR MAKING THE SAME

5 **FIELD OF THE INVENTION** – The present invention relates to the field of ceramic propping agent, preferably for use in oil and gas extraction. The present invention also relates to the field of foundry sands.

10 **ABSTRACT** – The present invention describes a method for producing bulk, particulate high crush strength, and inert ceramic materials with a quasi-spherical shape prepared from raw oxide residues. These oxide residues are produced from the regeneration of spent acids based on a pyro-hydrolysis process, and/or as by-products from mineral processing and ore beneficiation operations. The final solid granules are obtained from the thermal treatment
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25 metallurgical industry.

STATE OF PRIOR ART AND BACKGROUND OF THE INVENTION -

Under constant market and prediction of long term depletion of hydrocarbon resources, the oil and gas industry has constantly sought to increase the productivity of gas and crude oil wells. As a result, drilling depths have
5 increased in order to efficiently recover oil and gas from existing and/or new oil fields which were originally thought to be inaccessible.

Several techniques were specifically developed in order to improve the recovery of crude oil and natural gas from shallow and poor deposits not
10 easily accessible in the past. Among these methods, the best-known techniques of reservoir beds treatment are the fracturing technologies. Two methods basically exist for extensive improvement of the inflow conditions in a reservoir bed¹: **hydraulic fracturing**, and **pressure acidizing**.

15 The hydraulic fracturing technique was developed by the oil industry in the 1940's for opening up tight reservoir rocks to improve product recovery. It consists of pumping and injecting a frac fluid (i.e., water or brine) into the production well until the hydrostatic pressure increases to a level sufficient to expand the strata and fracture the rock which results in the creation of a
20 network of cracks into the rock formation. The fractures produced are generally only a few millimetres wide, but may be either horizontal or vertical depending on the path of least resistance. With a widening fracture, the oil increasingly migrates into the pore space of the rocks. Therefore the presence of high conductivity fractures affects the overall oil mass transfer
25 efficiency, and they have a significant impact on the reservoir performances.

¹ from H. Rischmuller - *Resources of Oil and Gas* - in *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A23 VCH Publishers, Inc., Weinheim Germany (1993) pp. 183.

In order to insure the success of reservoir beds treatment, a sufficient depth of the penetration must be achieved. After the porous rock has been fractured it is necessary to prop open the newly formed cracks in order to facilitate the continued flow of gas and oil and to avoid the catastrophic
5 collapse of reservoir walls due to the elevated surrounding lithostatic pressure. If this was not done, the newly formed cracks would close under the overburden. The common technique consists in pumping slurry made of a mixture of fluid and solid particulate materials into the fractured formation. The particulate materials are specifically named *propping agent* or *proppants*.
10 Therefore, proppants are agents that maintain the cracks open, avoid the collapse of reservoir wall and insure an efficient mass transfer for both oil and gas. Noteworthy to mention, hydraulic fracturing, is not only used in oil and gas industry but also in hydrogeology to improve the performances of aquifers.

15 The second common technique is pressure acidizing, a particular method of hydraulic fracturing. The method consists of using an acid solution instead of brine or water as frac fluid. Actually, the increase of permeability versus common hydraulic fracturing is achieved by chemical dissolution of a part of
20 the carbonated matrix along the fracture faces. Obviously, this technique can only be used in the case of carbonated rocks, such as limestone, or dolomite. The most common acidic agents are aqueous solutions of hydrochloric acid (5-15wt. % HCl), hydrofluoric acid (1-6wt. % HF), acetic acid, citric acid, and surfactants. The *surfactants* are used as *dispersing agents* in order to
25 promote the dispersion of the solids, to improve the wettability of the rock, and to prevent emulsification.

As a general rule, not all the classes of materials can be used as propping agent. Actually, due to the existing geothermal gradient (e.g., 30°C/km) and lithostatic pressure (e.g., 20 MPa/km), suitable proppant materials must withstand both these harsh conditions (i.e., high temperature and elevate
5 pressure present at the bottom of the well) encountered in deep wells (up to 6 km), and insures a good mass transfer of oil (i.e., offers a high permeability). Hence, the critical characteristics and properties that a proppant must meet in order to be considered industrially are listed below:

- ✓ High crushing or compressive strength,
- 10 ✓ Elevate gas and oil permeability,
- ✓ Narrow particle size distribution,
- ✓ Low specific surface area,
- ✓ Low bulk and tap densities,
- ✓ Chemical inertness in hot acidic solutions and hot brines,
- 15 ✓ Good thermal stability,
- ✓ Good flowability and rheology in frac fluids,
- ✓ Low abrasiveness,
- ✓ Low cost and large availability.

Thus, it is an object of the present invention to provide such a material
20 at a competitive price.

In order to select and quickly rate a suitable propping agent, the material must be characterised according to well known standards published by the *American Petroleum Institute (API)*.

25 The main materials commonly used industrially as proppants can be grouped into three main categories: (1) rounded silica sand, (2) resin coated gravel and sand, and (3) sintered and fused ceramics.

- (1) Rounded silica sand (e.g., from Oglebay) is from an historical point of view, the first proppant material used. This naturally occurring material is usually mined from glacial deposits (sometimes called Ottawa's sand) and is essentially is made of quartz grains (SiO_2). Silica sand was selected owing to its wide availability, low density, chemical inertness, and its low cost and until today it remains the major proppant material consumed worldwide (80% of the proppant market). Nevertheless, several drawbacks such as a low permeability, a low crushing strength that restrict its use in the range of 28-35 MPa, and poor resistance to flowback have conduct oil producers to prefer other materials for the deepest wells. Therefore several synthetic materials were selected and now used as propping agents and today we observe the increased use of these synthetic proppants.
- (2) Resin coated and impregnated gravel and sands (e.g., Santrol) are particulate materials coated with a phenolic resin. The concept was to inject a partially cured resin coated proppant into a well and let the elevated bottom hole temperature finish the resin polymerisation and bond the coated particles together forming a downhole filter. By resin coating a proppant with a phenolic formaldehyde resin that is securely attached to the proppant surface by a silane or other coupling agent, the former brittle material becomes crush and acid resistant and improved backflow. But the use of these materials is already restricted to a pressure range of 35 to 69 MPa. Hence, in order to meet the demand of high compressive strength and elevate permeability required in the deepest wells, new ceramic proppants materials were produced.

- (3) Ceramic proppants are modern synthetic materials usually made by firing, melting, or sintering of bauxite² and kaolinite [$\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$, triclinic] clay³⁴. After processing the final material mineralogical composition consists to a mixture of mullite [$(\text{Al}_4(\text{SiO}_4)_{10})_2\text{Al}_2\text{O}_3$, orthorhombic]⁵ and corundum [$\square\text{-Al}_2\text{O}_3$, rhombohedral]. However in some rare cases they can also be prepared from other fused ceramic materials : silicon carbide (SiC), mixture of yttria or ceria-stabilised cubic zirconia and hafnia ($\text{Y}_2\text{O}_3\text{-CeO}_2\text{-ZrO}_2\text{-HfO}_2$)⁶⁷, zircon (ZrSiO_4), and other exotic materials. Synthetic ceramics materials (e.g., Carbo-Ceramics Inc.) offer the highest crushing strength allowing them to be used until 140 MPa, chemical inertness, but they exhibit a high density that required viscous carrying frac fluids leading to higher pumping rates and increase in brake-power, in addition their relatively elevated cost restricts their use in certain conditions where other proppants are not satisfactory.
- 15 Synthetic proppant materials are produced industrially according to several granulation-processing routes currently used in the ceramics industry for producing beads, and other particulate materials. Among these granulation processes :(1) granulation by agitation : fluidizing, tumbling, and mixing, (2) granulation by pressure : pelletizing, extrusion, and rolling, and (3) granulation by spraying : atomization, and flame spraying, are the most

² W.H. Andrews (Comalco Aluminium Limited, Melbourne, Australia) – *Bauxite Proppant* - U.S. Pat. 4,713,203; Dec. 15 (1987)

³ H.M. Bourne, and P.A. Read (AEA, U.K.) – *Well Treatment* – U.S. Pat. 5,964,291; Oct. 12 (1999).

⁴ L. Sweet (Carbo Ceramics Inc., Dallas, TX, USA) – *Method of Fracturing a Subterranean Formation with Lightweight Propping Agent* - U.S. Pat. 5,188,175; Feb. 23 (1993).

⁵ F. Cardarelli (2000) – *Materials Handbook* – Springer-Verlag, New York and London, pages 437 and 444.

⁶ D. Urffer (Soc. Europ. des Produits Réfractaires, Neuilly-sur-Seine, France) – *Propping Agent based on Zirconia and Silica for Deep Geological Fractures* – U.S. Pat. 4,607,697; Aug. 26 (1986).

⁷ C. Bert, and D. Urffer (Soc. Europ. des Produits Réfractaires, Courbevoie, France) – *Fused Ceramics Beads* – U.S. Pat. 5,502,012; Mar. 26 (1996).

common methods described in the technical and patent literature⁸. Although, the various ceramics proppants described in the prior art are of good quality, higher productivity required new ceramics proppant materials capable to withstand harsh conditions find in downhole drilling and meeting efficiency requirements such as high permeabilities, and low densities.

DESCRIPTION OF THE INVENTION - The raw materials used in this invention are solid oxide residues produced as by-products of an acid regeneration plant (ARP) for the recovery of spent aqueous solutions containing hydrochloric acid, sulphuric acid, or nitric acid or their mixtures. For example, the raw material can be obtained from the ARP plant used for extracting impurities from titanium slags.

These solid residues that could be produced in form of pellets, granules, powders, dusts, ashes, and nanometric particles are composed of numerous oxides not limited to: iron oxides, aluminium oxide, chromium oxides, cobalt oxides, manganese oxides, titanium oxides, zirconium oxide, vanadium oxides, magnesium oxide, calcium oxide, sodium oxide, potassium oxide, copper oxides, nickel oxides, silicon dioxide, and miscellaneous rare earth oxides.

These oxide residues can be produced from the recovery of the above mixture of spent acid by means of a pyro-hydrolysis process using a fluidized-bed reactor. The reactor is continuously fed with spent acid and hot gases and generates the solid oxide residues and fresh acids. Afterwards, the acid is

⁸ R.B. Castle (3M Company, MN, U.S.A.) - *Composition Comprising Fused Particulates and Methods of Making Them* - U.S. Pat. 5,883,029; Mar. 16 (1999).

reused in the process, while oxide residues are processed in order to obtain granules with desirable properties suitable to be ready to use as proppants or foundry sands.

- 5 Several techniques can be used to transform crude residues into the final granules. However, prior to be processed as final granules, the solid oxide residues can be pretreated in several ways: (1) impregnated with an aqueous concentrated solution of alkali-metals silicates (e.g., sodium or potassium silicates) and air-dried, (2) mixed with minerals or materials found as
10 common by-products in the mining industry such as gangue minerals: feldspars (e.g., orthoclases, and plagioclases), micas, quartz, amphiboles, pyroxenes, calcite, fluorspar, gypsum, barite, kaolinite, clay, or dust collected in flue gases, (3) mixed with additives such as surfactants or with fluxing agents: e.g. cryolite. These pretreatments will allow to facilitate the
15 vitrification process, i.e., the formation of a glassy layer at the surface of particles rendering its surface smoother and increasing the roundness index. Afterwards, the pretreated or raw residues are submitted to a final granulation process. Several processes are used for that purpose:
- 20 **Atomization** – This technique involve the melting of raw materials particles together in order to obtain a molten bath of bulk liquid. Usually, the bulk liquid contains more than thousands of times the amount of raw materials required to make a single product particle. A thin stream of molten material is atomized by dropping it into a disruptive air jet thereby subdividing the
25 stream into fine, molten droplets. The droplets are then kept away from one to another and from objects until they have been cooled and solidified. Then

they can be recovered as substantially discrete ellipsoidal glassy (i.e., amorphous) particles.

Fire-polishing – In this techniques, discrete solid residues particles are
5 heated to the softening or melting temperature of the material while
suspended and dispersed in a hot gaseous medium (e.g., fluidized bed
reactor). As particles become soft or molten, surface tension forms them to
exhibit an ellipsoidal shape. If kept in suspension until cooled below
softening temperature, the particles may be recovered as discrete glassy
10 ellipsoids.

Tumbling - In this technique, discrete solid residues particles are heated to
the softening or melting temperature of the material while gently rotated into
a rotary furnace. Firing can be provided by electric heating, induction
15 heating, infrared heating, or gas combustion (i.e., kilns). As particles become
soft or molten, surface tension forms them to exhibit an ellipsoidal shape,
and the rotation displacement avoid the adhesion of particles together
avoiding the formation of a clinker. If kept in rotation until cooled below
softening temperature, the particles may be recovered as discrete glassy
20 granules.

Flame-spraying – In this technique fine ground raw particles are pre-mixed
with a combustible gas mixture, i.e., fuel and oxidant, and the mixture is then
introduced into a burner. Hence, in the hot flame, the tiny particles melt or
25 soften, and the surface tension leads them to exhibit an ellipsoidal shape. In
order to prevent molten droplets or soften particles to contact any surface
before cooling the flame must be allowed to move freely in a large

combustion chamber. The droplets or soften particles are then kept away from one to another and from reactor walls until they have been cooled and solidified. Then they can be recovered as substantially discrete ellipsoidal glassy (i.e., amorphous) particles.

5

In order to assess the final performances of the materials a comparative testing with commercially available proppants purchased from different producers were achieved. Close examination of Table 1 shown below demonstrates the ability of the materials described in this invention to be use
10 as a high performance and long lasting proppant material that could overcome all the drawbacks of commercially available products at a reduced cost.

The end-uses of the products of the present invention that are described
15 above are those which presently appear most attractive (i.e., proppants, and foundry sands). The foregoing disclosures of embodiments of the invention and end-uses therefore have been given merely for purposes of illustration and not to limit the invention. Thus the invention should be considered to include all embodiments falling within the scope of the following claims and
20 equivalents thereof.

Table 1 - Comparison of QIT proppants with commercial proppant for the 20/40 meshes size fraction

Proppant type	Density (ρ / kg.m ⁻³)		Crushed fraction @ 69 MPa (x / wt.%)	Weight loss (wt.%) @ 60°C (or 100°C)		Permea- bility ⁹ (121°C) (k/D)	Conducti- vity ⁹ (121°C) (k/mD-ft)	Porosity (ϕ vol.%)	Roudness index (RJ)	Sphericity (ϕ)	Cost (\$/tonne)
	tap	bulk		HCl-HF	boil. water						
• Rounded silica sand (Oglebaynorton)	1,540	2,650	6.7 (28 MPa)	0.9	traces	58	952	0.6	0.6	0.9	50 - 155
• Resin coated sand (Santrol)						160	3,000				200 - 600
• Low cost and light weight ceramics (CARBO- ECONOPROP®)	1,570	2,710	5.2 (42 MPa)	1.7	traces	340	2,000	0.9	0.9	0.9	422 - 556
• Lightweight and intermediate strength ceramics (CARBOLITE®)	1,620	2,710	8.3	1.7	traces	340	6,000	0.9	0.9	0.9	333 - 480
• Intermediate strength ceramics (CARBOPROP®)	1,880	3,270	5.1	4.5	traces	290	4,450	0.9	0.9	0.9	333 - 480
• High strength sintered bauxite ceramics (CARBOHSP®2000)	2,040	3,570	0.7	3.5	traces	1,609	23,462	0.9	0.9	0.9	650 - 880
• QIT oxide granules	2,000	2,600	0.5	1.0	traces	2,000	25,000	0.9	0.9	0.9	500

⁹ At a closure stress of 42 MPa (6 ksi)

Claims :

1. A method for the manufacture of granules comprising the steps of : (i) preparing the solid oxide residues in form coarse grains, pellets, powders, ashes, dusts, nanometric particles by regenerating spent acids from ore processing using a pyro-hydrolysis process based on a fluidized bed reactor. (ii) pretreating the raw oxide residues by impregnation with a concentrated aqueous solution of alkali-metals silicates (e.g., potassium and sodium silicates), adding gangue minerals by-produced from ore beneficiation processes such as : feldpars (e.g., orthoclases, and plagioclases), micas, quartz, amphiboles, pyroxenes, calcite, fluor spar, gypsum, barite, kaolinite, clay, dust and ashes from flue gases, mixing with fluxing agents : cryolite, periclase, or adding additives such as surfactants. Granulating the residues by techniques such as tumbling, mixing, pelletizing, flame-spraying, atomization, or spray-drying.
2. The method of claim 1 wherein solid oxide residues are produced as mining residues or as by-products of spent acids regeneration plants and/or ore beneficiation plants.
3. The method of claim 1 wherein spent acids can be hydrochloric, hydrofluoric, sulphuric, nitric, phosphoric or a binary, ternary, quaternary mixture of them.
4. A granular material having a mineralogical composition comprising between wt.% Fe_2O_3 , wt.% Al_2O_3 , wt.% MgO , wt.% CaO , wt.% TiO_2 , wt.% ZrO_2 , wt.% Cr_2O_3 , wt.% V_2O_5 , wt.% Co_2O_3 , wt.% NiO , wt.% MnO , wt.% FeO , wt.% Na_2O , wt.% K_2O , wt.% Ln_2O_3 (with Ln = Rare Earths Metals), and wt.% SiO_2 .
5. The material of claim 4 wherein said mineralogical composition and crystallographic structure made of spinel group minerals having the basic formula X_2YO_4 with X = Fe(II), Mg, Ca, and Y = Fe(III), Cr(III), Al, and lanthanides.
6. The material of claim 4 in the form of solid particles having a pycnometric density ranging between 1,500 and 3,500 kg.m^{-3} , preferably between 2,500 and 3,000 kg.m^{-3} , more precisely between 2,700 and 2,800 kg.m^{-3} .
7. A composition of matter comprising solid particles having a tap density ranging between 1,500 and 2,500 kg.m^{-3} , preferably between 1,600 and 2,400 kg.m^{-3} , more precisely between 1,700 and 2,300 kg.m^{-3} .
8. A composition of matter comprising solid particles having a narrow particle size distribution ranging between 10 and 140 meshes (i.e., between 0.1 mm and 2.0 mm), preferably between 16 and 60 meshes (i.e., between 0.250 mm and 1.180 mm), more precisely between 20 and 40 meshes (i.e., between 0.425 mm and 0.850 mm).

9. A composition of matter comprising solid particles having a crushing strength ranging between 10 and 2,000 MPa, preferably between 50 and 1,000 MPa, more precisely between 80 and 200 MPa.
- 5 10. A composition of matter comprising solid particles having a permeability coefficient ranging between 10 and 5,000 darcies, preferably between 50 and 4,000 darcies, more precisely between 800 and 2,000 darcies.
- 10 11. A composition of matter comprising solid particles having conductivity coefficient ranging between 500 and 50,000 darcy-feet, preferably between 1000 and 30,000 darcy-feet, more precisely between 5,000 and 25,000 darcy-feet.
- 15 12. A composition of matter comprising solid particles having a weight loss in the acidic mixture made of 12wt.%HCl-3wt.%HF expressed in mass fraction ranging between 0.01 and 30wt.%, preferably between 0.1 and 10wt.%, more precisely between 0.5 and 2wt.%.
- 20 13. A composition of matter comprising solid particles having a weight loss in the boiling water expressed in mass fraction ranging between 0.001 and 5wt.%, preferably between 0.01 and 1wt.%, more precisely between 0.1 and 0.5wt.%.

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